ChE curriculum

TEACHING CHEMICAL ENGINEERING THERMODYNAMICS AT THREE LEVELS

Experience from the Technical University of Denmark

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According to the so-called "Bologna model," many technical universities in Europe have divided their degree programs into separate 3-year Bachelor's and 2-year Master's programs (followed by an optional Ph.D. study). Following the Bologna model, the Technical University of Denmark (DTU) has recently transformed its 5-year engineering program into a 3-year Bachelor (B.Sc.) and a 2-year Master's (M.Sc.) program. Master's graduates that are interested and have achieved a good grade average are then in principle qualified for a 3-year Ph.D. In addition to the above, DTU has a 3.5-year industrial Bachelor's program ("diplom" or B.Eng.), which directly qualifies its graduates for an industrial career. In all of these programs there are studies in applied chemistry and chemical engineering. Four different courses on chemical engineering thermodynamics are provided at the four levels mentioned above, thus satisfying the different needs of these programs. This manuscript discusses the different roles, context, teaching objectives, and educational methods used in the various courses. Examples are provided for all courses, with emphasis on the different types of exercises used. Finally, the suitability of thermodynamics textbooks for these courses is also discussed.

WHY 4 COURSES IN THERMODYNAMICS?

An evident question is why so many different courses are needed in "applied chemical engineering (technical) thermodynamics." The necessity for the four courses in thermodynamics will hopefully become apparent from the brief description of their characteristics, illustrated in Tables 1-3, and the description of their similarities and differences provided hereafter. In the discussion below, we follow the notation used in Table 1 for the courses, *i.e.*, A for the B.Eng., B for the B.Sc., C for the M.Sc., and D for the Ph.D course.

An important "common" characteristic of the four courses is that they all focus on aspects of thermodynamics that are of interest to chemical engineers. This characteristic differentiates them from more fundamental physical chemistry

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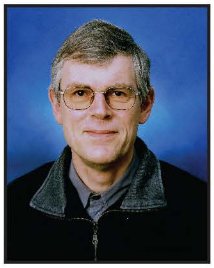

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TABLE 1
Four Degree Programs and Four Courses in Thermodynamics at DTU

Degree Program	Course Name	Suggested Semester
A. B.Eng. (industrial B.Sc.)	Chemical Engineering Thermodynamics	3
B. B.Sc.	Chemical Engineering Thermodynamics	4-6
C. M.Sc.	Phase Equilibrium for Separation Processes	> 7
D. Ph.D.	Thermodynamic Models: Fundamentals and Computational Aspects	—

TABLE 2
Comparison of Important Characteristics of the Four Thermodynamic Courses

Course/Program	Basic Objectives	Teaching Methods	Evaluation
A. B.Eng.	Estimation of physical-chemical properties for pure compounds and mixtures for use in chemical processes	Lectures Excel spreadsheets	Oral exam + projects
B. B.Sc.	Application of physical chemistry to solution of practical, industrial problems	Short lectures Excel spreadsheets using pre-developed modules that the students use and combine to simulate larger units and processes	Three projects on well-defined problems
C. M.Sc.	Presentation of thermodynamic models and theories for a wide range of fluid mixtures ranging from hydrocarbons and chemicals (and at both low and high pressures) to associating fluids, polymers, and electrolytes	Lectures Classroom exercises Available software with various models	One project at the end of the course based on research articles
D. Ph.D.	Fundamentals of thermodynamics, and how to program and debug fast and efficient computer codes for thermodynamic models and for a variety of advanced computational methods	Lectures Writing own programs	Final project requiring writing own Fortran code

TABLE 3
The Course Context of the Four Courses

Course	Course Context (in general lines)
B.Eng.	Equations of state for estimating properties (pure fluids and mixtures) including residual, partial molar, and excess properties. VLE, LLE and SLE calculations with activity coefficient models. Refrigeration and liquefaction processes. Phase diagrams for VLE/LLE/SVE as used for distillation and extraction processes. Colligative properties for binary mixtures.
B.Sc.	Same as for B. Eng., except for the colligative properties. Added are: compression processes, discussion of the assumption behind the choice of models, derivation of expressions for fugacity, enthalpy and entropy from a given EoS, and parameterization of cubic EoS
M.Sc.	Intermolecular forces. Cubic Equations of state with classical and advanced (EoS/G^E) mixing rules. Random-mixing and local composition activity coefficient models. Corresponding States, group contributions and regular solutions. Association theories (CPA, SAFT). Phase diagrams and models for electrolytes and polymers—emphasis on free-volume concepts. Environmental thermodynamics.
Ph.D.	Fundamentals (state functions, equilibrium and stability, reference states, electrolytes, derivatives of thermodynamic functions, checking models for consistency). Models (equations of state, activity coefficient models, Debye-Huckel, ion exchange, adsorption equilibria). Computational methods (PT-flash: successive substitution, Rachford-Rice, higher order methods. Multiphase flash. General state function based specifications. Dew- and bubble-points, stability analysis, and the calculation of critical point. Chemical equilibrium calculation)

In terms of use of textbooks, only course D employs a specific textbook.[1] Courses A-C are based on the authors' own teaching notes, but some recommended teaching is proposed.[2-3] In Table 4, various recent thermodynamic textbooks are discussed, from the point of use of the programs of DTU. Despite the many positive features of all of these textbooks, we feel that none is suitable for all the purposes. For example, several of these textbooks do not contain chapters on polymer or electrolyte thermodynamics, environmental applications of thermodynamics, or the newest developments in equations of state—*e.g.,* association models (SAFT, etc) and the EoS/G^E mixing rules. These remarks by no means constitute criticisms of these excellent textbooks, rather an observation in relation to the needs of the courses taught at DTU. We do recommend several of these textbooks as supplementary reading material.

courses. Moreover, all of them put emphasis on "applied ways of learning," but there are important differences both in the teaching methods employed and the level of difficulty, as will be explained later.

The audience of the three courses and also their interests and expectations from a course in thermodynamics are different. Only the B.Eng. (A) course is mandatory, while all the other courses (Bachelor, B; M.Sc., C; and, of course, the Ph.D. course, D) are elective. B.Eng. students, in particular, expect a brief "to-the-point" course that they can use almost immediately in relation to other courses in their (chemical engineering) degree, and naturally later in their future employment, *e.g.*, in the oil and gas and chemical industries. Since this course is mandatory and also at an early stage (third semester), it must remain relatively simple and appealing to broader audiences (including students with interest in biotechnology), while providing all the aspects of technical thermodynamics expected from a mandatory course. The students should also understand the role of thermodynamics in central disciplines of chemical engineering, especially separation processes and process design. B.Eng. students may not take more advanced courses in thermodynamics, so the A course should provide them with all the necessary background to build on when required.

The B.Sc. course is taken by students in the Chemistry/Chemical Engineering B.Sc. program (called "Chemistry and Technology" at DTU) and although elective, it is typically chosen by students in their fourth to sixth semester. It is also a basic course, but because the B.Sc. education—unlike the B.Eng.—is not an independent education but rather a preparation for the more advanced M.Sc. studies, several of the B.Sc. students may wish to take a somewhat more advanced course than the B.Eng. All the B.Sc. students will have taken, prior to attending course B, one or two courses in physical chemistry, and moreover they may, at a later point, choose to take course C (during their M.Sc. studies). Based on the rather loose structure of B.Sc. studies at DTU, the students who choose the B.Sc. course B may not have a "complete idea" of the role of thermodynamics in chemical engineering and will typically only take courses on process design and separations later in their M.Sc. studies. Most of the B.Sc. students taking course B will have interests in chemistry/chemical engineering but not so much in biotechnology, as the latter would take another bachelor-program line.

The M.Sc. course C has as a prerequisite one of the above courses (A or B), and builds from those. The audience of this course, however, is much broader, with not only students from chemistry and chemical engineering but also students from petroleum engineering, polymers, and environmental engineering (but, in general, not from Biotechnology). Thus, the thermodynamic models/methods and types of mixtures that should be covered and students' expectations from course C are much broader.

Finally, the Ph.D. course builds also on courses A or B. A C-type course is not a prerequisite for the Ph.D. course but it may be useful. The Ph.D. course emphasizes computational aspects of thermodynamic models and phase equilibria calculations, and the students are then able to understand and write computer programs for phase equilibrium calculations including all sensitive aspects of stability and flash calcula-

TABLE 4
Discussion of Thermodynamic Textbooks

Textbook	Recommended for the course	Characteristics
Elliott and Lira[2]	B, C (partially)	Excellent new textbook. Includes exercises and also some advanced topics (association models). Nice discussion of local composition models and links between some models. Worked-out examples, software available.
Prausnitz, *et al.*[4]	C	Classical textbook—now in its 3rd edition. References to numerous models including the newest approaches. Includes chapters on polymers, electrolytes, EoS/G^E mixing rules. Somewhat confusing presentation of far too many models and missing unified presentation of the different approaches.
Tassios[5]	A,B,C (partially)	Older textbook. Clear presentation of classical topics in thermodynamics including certain advanced topics (intermolecular forces, development of cubic EoS, statistical mechanics).
Vidal[6]	A,B,C (partially)	New textbook with emphasis on oil applications, *e.g.*, characterization, solids (wax, hydrates) are included. Chapters on EoS/G^E mixing rules and polymers.
Israelaschivili[7]	Supplement to C	Excellent discussion of intermolecular (Part 1) and interparticle/interfacial forces in Colloids (Part 2)
Smith, *et al.*[3]	A,B,C (partially)	Classic in the field, now in its 8th edition. Includes chapters on intermolecular forces and certain advanced topics, *e.g.*, on solid-gas equilibria.
Sandler[8]	A,B,C (partially)	Interesting textbook with worked-out examples and certain advanced topics such as EoS/G^E mixing rules. Somewhat confusing nomenclature.
Kontogeorgis and Gani[9]	C (supplement)	Chapters on several advanced topics (EoS/G^E mixing rules, associating models, polymers, electrolytes, etc.). Not written in textbook form for students and expensive for use in universities.

TABLE 5
Course Layout of "Chemical Engineering Thermodynamics for Industrial Bachelor's" (Course "A")

No. of 4-hour modules	Topics	Type of Exercises
2	Pure components, Residual properties. Process applications	Excel exercises: Van der Waals EOS PR/SRK EOS (using pre-programmed macros)
2	Partial properties. Activity	Classroom pocket calculator
3	Phase diagrams, VLE/LLE/SLE	Classroom pocket calculator
2	VLE models: Ideal mixtures Activity models (Wilson, NRTL)	Excel exercises: Dew- and bubble-point calculations, flash calculations (using pre-programmed Wilson/NRTL macros)
1	LLE calculations: NRTL	
1	Colligative properties	Excel exercises: Freezing curve
2	—	Project work (mainly Excel)

tions in complex situations.

As could be anticipated from the above presentation, the degree of difficulty (and also student initiative) rises from level A (B.Eng.) to D (Ph.D.), with courses A and B being rather close in both level and expectations (although under the assumptions discussed above). The students work on small projects in courses A and B and employ pre-programmed modules in Excel, typically with the thermodynamic models they should be using specified from the start. The students actively combine elements such as activity coefficients and vapor pressures to arrive to the final results.

In course C, software is used that contains numerous thermodynamic models and tasks (see more detailed description later), and student selection of appropriate models for specific applications and evaluation of results is expected, along with an in-depth understanding of the derivation and theoretical background of the models. Finally, at the final level (course D), students write their own codes, having been given basic thermodynamic codes (including derivatives) to start.

Following the general comparative description of the context and needs of the four courses presented in Tables 1 through 4, we will now present their most important characteristics with some special emphasis on the educational methods and the software and other tools employed.

ChE THERMODYNAMICS FOR INDUSTRIAL BACHELOR'S (COURSE "A")

This is a new course that was taught for the first time in the Fall of 2006. The course is compulsory for the B.Eng. degree and is given jointly by the Department of Chemistry and the Department of Chemical Engineering. One-third of the course is devoted to physical chemistry (phase diagrams, activity, partial and excess properties, colligative properties). The rest of the course is traditional chemical engineering thermodynamics with more emphasis on the application aspects and less on theory. The thermodynamic content of this course is therefore somewhat smaller than that of other "traditional" thermodynamics courses, *e.g.*, Course "B" for B.Sc. students.

The general objective of this course could be summarized as follows: Sizing and optimization of process units (distillation, extraction, compression, cooling, etc.) requires thorough knowledge of the thermodynamic properties of the chemical species (pure/mixture) present. Physical chemistry provides the theoretical framework, which makes the calculation of these properties possible with approximate models, even with limited availability of experimental data. The goal of this course is to enable the participants to estimate thermodynamic properties of pure species and mixtures for application in sizing and optimization of process units.

A more detailed description of the content of the course is shown in Table 3, while the course layout and distribution of the various topics in the 13 4-hour modules devoted (at DTU) for a 5 ECTS point course is shown in Table 5.

The students are evaluated based on reports they write in small groups (three to four students) on three topics

(i) *Ammonia cooling circuit:* Sizing of an ammonia compressor cooling circuit for cooling fermentor broth to 10 °C.

(ii) *Binary mixtures Vapor-Liquid:* Calculation of partial and excess molar volumes based on experimental data-Calculation of phase diagrams (Pxy) given experimental data assuming either ideal behavior or an activity coefficient model (Wilson equation).

(iii) *Freezing point depression, LLE extraction:* Calculation of freezing curves for a binary mixture (pure solid phase only). Calculation of the compositions of the two liquid phases for ternary mixtures.

Several of these problems are similar to those used in Course "B" and are described in the next section. Both during the course and in the above-mentioned project, Excel is used extensively (see also next section). Excel is a versatile tool that the students most likely will use in their professional careers, and more than 90% of engineers frequently use Excel for solving engineering problems, actually many more than those using commercial process simulators,[10] according to a recent investigation of CACHE.

PROBLEM SOLVING IN ChE THERMODYNAMICS (COURSES "A" AND "B")

The general concept—use of Excel in thermodynamics

Classical textbook problems in chemical engineering thermodynamics of the type:

> *"Carbon dioxide is compressed adiabatically from 300K, 1 Bar, to an outlet pressure of 4 Bar. Calculate the outlet temperature, assuming isentropic compression and ideal gas behaviour with a constant heat capacity . . . ."*

solved with pen and paper and a pocket calculator, tend to bore students. One may, of course, make the problem more realistic by incorporating a temperature-dependent heat capacity. In itself, this does not really make the problem more fun to solve.

Much more interesting possibilities arise with the use of computers and easy-to-use tools such as spreadsheets. The above problem, for example, is easily solved with the spreadsheet PREOS.XLS from the textbook of Elliott and Lira,[2] where an appropriate EoS (equation of state, in this case Peng-Robinson) allows us to solve the problem rigorously, without simplifying assumptions.

In our basic thermodynamic courses, the students solve three major problems, as also shown in the previous section for the B.Eng. course. In the case of the B.Sc. course, two of the projects are described below.

Problem related to "pure components"

The first project has carbon dioxide as its topic. Data are retrieved from NIST, and the students use Excel to derive Clausius-Clapeyron (by plotting lnP vs. 1/T) parameters and next Antoine parameters (by nonlinear regression, using Excel's solver) for the vapor pressure of CO_2. Next they investigate, by comparing to the data for NIST, at what temperature and pressure ranges the gas phase can be calculated as ideal, and for a number of isotherms the data are also compared with those found using the van der Waals (vdW) equation.

Experimental vapor pressures are then compared with those calculated from the Peng-Robinson equation by means of PREOS.XLS. The students are then required to modify the spreadsheet such that SRK is used instead and to compare the results with what this EoS gives (which is virtually identical to that of PR). Finally, they have to modify the spreadsheet to use vdW, which essentially is shown to be useless for the vapor pressure calculation.

For the final part of the first project, the students have to optimize a sequence of compressors with intercooling. Carbon dioxide has to be compressed from 1 Bar, 300 K, to 80 Bar in two, three, or four stages, with cooling to 300 K after each compressor. The objective is to determine the intermediate pressures such that the total work is minimized. PREOS.XLS can, of course, easily be used to calculate a single stage compression by

1. *Calculating S and H at inlet conditions.*
2. *Solving for the outlet temperature where outlet entropy matches inlet entropy.*
3. *Calculating the enthalpy at outlet conditions.*
4. *Calculating the isentropic work as the enthalpy difference.*
5. *Calculating the real work as the isentropic work divided by the efficiency.*

For a two-stage cascade it is possible to guess the intermediate pressure, calculate the work for each of the two steps, and by trial and error adjust the intermediate pressure to arrive at the minimum work. This process is tedious, however, and difficult to extend to additional stages.

We, therefore, supply students with an Excel module, written in Visual Basic, that has the same functionality as PREOS.XLS but can be called as an ordinary Excel function anywhere in the spreadsheet (all spreadsheets used in the course are available from the authors upon request). Actually, two routines are used:

1. An initialization routine,

=Cub_Ini(Mod,Tcr,Pcr,Omega,Cpcoef),

where Mod is a code for the model (PR or SRK), Tcr, Pcr ,and Omega are critical temperature and pressure, and acentric factor for the compound, and Cpcoef are coefficients giving

TABLE 6
Course Layout of "Phase Equilibria for Separation Processes" (M.Sc. course, C)

No. of 4-hour modules	Topics	Specifics
2	Phase diagrams—Basic relationships—Intermolecular forces	—
4	Classical models	Cubic equations of state with vdW1f and EoS/G^E mixing rules. Random-mixing and local composition activity coefficient models incl. group contributions.
1	Environmental thermodynamics	Octanol-water partitioning. Distribution of chemicals in environmental ecosystems.
3	Electrolyte thermodynamics	Standard states. Nernst equation, osmotic coefficients, and activity coefficient models.
1.5	Polymers	Phase diagrams. Basic approaches (solubility parameters, Flory-Huggins) and free-volume models. Equations of state.
1.5	Association models	SAFT and CPA—applications to petroleum, chemical, and polymer industries.

the ideal gas Cp as a temperature polynomial.

2. A calculation routine, =**Cub prop(T,P,X)**, where T and P are the actual temperature and pressure, and X is a text string specifying the property to calculate, *e.g.*, "HL" for liquid enthalpy.

It is now possible to formulate the calculation of the compression cascade as a constrained optimization that can be solved in a single step by the solver in Excel. For a three-stage compression, we have

- *5 Decision variables: The 3 outlet temperatures and the 2 intermediate pressures.*
- *One objective function: The total work,* i.e., *the isentropic work, corrected by the compressor efficiencies.*
- *3 Constraints: The condition of outlet entropy for the isentropic compression being equal to the inlet entropy.*

There is no problem in determining the solution as long as suitable initial estimates are available. And here, the "classical" approach with the ideal gas, constant heat capacity assumption becomes useful, with its analytic solution to the problem.

What we gain by this approach is the following:

1. *We are able to solve quite realistic problems without using tools where the students just have to "fill in the numbers."*
2. *The aid in form of the Excel module is transparent. The students can see the same thing done in PREOS.XLS and the module just represents a different and more useful, although less flashy, packaging.*
3. *The creative element of formulating the conditions and setting up the equations to be solved is still left to the students.*

Problem related to mixtures

The final course problem has mixtures and equilibrium calculations as subject. For this problem, a new Excel module is provided, with the following capabilities for multicomponent mixtures:

1. *Activity coefficient models. We provide the following:*
    - *Wilson*
    - *UNIQUAC*
    - *NRTL*
2. *Equations of State for mixtures. We provide the following:*
    - *Soave-Redlich-Kwong*
    - *Peng-Robinson*
3. *A Rachford-Rice equation solver.*

The property routines include an initialization part in which the model parameters (*i.e.*, interaction energies and size parameters for the activity coefficient models, critical properties, and interaction coefficients for the equations of state) are specified, and a calculation routine that given composition and temperature returns a vector of activity coefficients (for the activity models), or given composition, temperature, pressure and liquid state returns a vector of fugacity coefficients for the equations of state. Finally the Rachford-Rice function returns, given a composition vector and a K-factor vector, the vapor composition.

These tools are used for solving the following problems:

- *Calculating nonideal Pxy and Txy-diagrams.*
- *Calculating an ideal solution PT-flash.*
- *Calculating PT-flash using an EOS for the model description.*
- *Regressing energy parameters from experimental Pxy or Txy-data for a binary mixture.*
- *Constructing a ternary type I diagram using an activity coefficient model with specified parameters.*

The nonideal flash is solved by successive substitution, as follows:

- *Initial estimates for the K-factors are calculated.*
- *The Rachford-Rice equation is solved.*
- *New compositions are calculated.*
- *New properties (activity or fugacity coefficients) are calculated that yield new K-factors.*
- *If calculated K-factors agree with assumed, terminate; Otherwise repeat from second step.*

This requires that we set Excel to permit iteration. Initially students are instructed to set the maximum iteration count to 1 to see how rapidly convergence occurs. The back-substitution of the calculated K-factors to the assumed is accomplished by means of a flag that selects the assumed K-factors either from the calculated or from the initial estimates. This enables an easy restart when things go wrong. For calculating the ternary diagram, the students start by specifying a feed containing equimolar amounts of the two immiscible components. The nonideal flash is used to calculate the corresponding equilibrium compositions, which yields one tie-line. Then, a small amount of the miscible component is added to the feed, and a new flash is converged. This process is continued until the entire diagram is calculated. In the process it becomes necessary to adjust the proportions of the immiscible components to not exit prematurely, too far from the plait point.

The setup gives the students a very good feel for the difficulties in doing calculations in the vicinity of the plait point. Even when the iteration count is increased to 1,000, the calculation often has to be repeated several times to converge, and the feed specification frequently is in the single-phase region, resulting in convergence to the trivial solution of phases of equal composition.

THE COURSE "PHASE EQUILIBRIA FOR SEPARATION PROCESSES" (M.Sc. COURSE, C)

Table 6 presents the course outline of the MSc course.

We have found it particularly useful to employ varying forms of teaching methods in almost every one of the course's 13 4-hour blocks including short lectures (via PowerPoint presentations with notes available in advance to the students), classroom exercises, and computer exercises. The course material is currently being enhanced and prepared in the form of a textbook.[13] Different types of exercises have been employed in this course as well. These include simple derivations or pocket-calculator calculations, *e.g.*, illustrations with activity coefficient models, polymer solutions, or derivations of EoS/G^E mixing rules and association schemes for novel association models, up to the somewhat more advanced applications—*e.g.*, those where equation of state calculations are involved that are performed using an in-house software package (SPECS). This software resembles the thermodynamic part of a process simulator in the sense that students can choose among a large variety of thermodynamic models, databases ("ordinary" systems, polymers, oil, electrolytes), and tasks (VLE, LLE) including, if necessary, different models for different phases and different mixing rules for the equations of state. Several up-to-date thermodynamic models are included (CPA, PC-SAFT, Entropic-FV for polymers, etc.).

The course is currently being taught in the present format for its sixth consecutive year, and based on student evaluations and other considerations, some enhancements have been made, including:

1. *The "introductory" part, i.e., the classical models including local-composition models and cubic EoS, includes several exercises aimed at illustrating similarities and differences among the various models but also strengths and weaknesses of the models, both from the theoretical and the application points of view. Although course C has courses A or B (or similar ones) as prerequisites, we have found that this structure also facilitates the understanding of complex concepts for students having different backgrounds, e.g., those from petroleum, polymer, or environmental engineering.*
2. *A topic addressed in the introductory lecture is the "needs of thermodynamic data and models," mostly from an industrial point of view. This is accomplished via references to selected articles written by colleagues from industry and in particular we have found the articles of Zeck*[11] *and Dohrn and Pfohl*[12] *to be particularly useful in this context, as example of one older and one more recent account of thermodynamic needs in the chemical industry.*
3. *Early in the course, a lecture is devoted to intermolecular forces and their application in understanding phase diagrams, as well as developing and understanding thermodynamic models. We constantly refer to the use of intermolecular forces in all subsequent lectures, including during the software and other exercises, e.g., when selecting models, interpreting phase diagrams. A multiple choice is used in this lecture to illustrate several aspects and "play around" with the various implications of intermolecular forces.*
4. *A lecture on "environmental thermodynamics" is included after the activity coefficient models, so that students encounter relatively early in the course a somewhat "different" but exciting application of thermodynamics.*
5. *The evaluation used in this course is a short project (individual or in small groups) provided during the last lecture, but based on the students' own choice of area of interest, e.g., oil & gas, polymers, electrolytes, environment, association theories (students are asked a week before to complete a relevant questionnaire). To ensure a satisfactory evaluation of the whole course, the evaluation will also include, besides the final project, exercises on selected sessions from the whole course.*
6. *The course project is based on one or more (recent) articles in the field of interest to the students (but chosen by the teachers) and the final report will include several components, e.g., summary of the articles, derivations, and calculations including using the software of the course. Critical discussion of models and results is typically included. The list of articles is continuously updated and students, in some cases, may provide suggestions for articles themselves, but even in this case, the choice and formulation of questions will be made by the instructors.*
7. *We have found it necessary to provide "overview" tables and summaries of the lectures outlining the most important messages (available upon request from the authors). Tables of "recommended models for specific types of applications (phase equilibrium calculations and separation processes)" have been also provided. One example is given in Table 7, while additional tables have also been provided outlining strengths and weaknesses of the models mentioned in Table 7. Of course such tables are not complete (they do not contain all available models) and they are necessarily somewhat biased or limited to the models covered in this course, but they provide a general picture of the different models or approaches needed/typically used for different applications.*

THE PH.D. COURSE

The objective of this course is that students become able to write robust and efficient computer programs for solving phase-equilibrium problems. An essential part of the course therefore is to implement the theory in algorithms of increasing complexity. Programming is done in Fortran.

We provide the students with precompiled modules for routine tasks such as solving sets of linear equations, and, in addition, with routines for calculating thermodynamic properties from a cubic equation of state. These routines contain a small component database of predominantly hydrocarbons. The students, given temperature, pressure, and molar amounts of the mixture species, are able to calculate volume and fugacity coefficients, and, in addition, the derivatives of these properties, with respect to temperature, pressure, and the molar composition.

The major part of the first week is used to build up a solver for the PT-flash. The students start by writing and testing a simple routine for solving the Rachford-Rice equation (calculation of vapor fraction, given K-factors and mixture overall composition). This routine is then used to implement a solution routine that uses successive substitution. In the next step, acceleration by the dominant eigenvalue method is implemented and tested, and finally, stability analysis is incorporated. The students who can find time for this conclude by implementing second-order methods.

The second week is used on more complex tasks. The first is to write a bubble- and dew-point routine, based on a partial Newton's method (where composition derivatives are neglected). This is followed by a phase envelope calculation where a full Newton method has to be implemented, and where the routines developed by the students are required to be able to pass the critical point of the mixture. The next problem is the multiphase flash, where the first step is the implementation of a general multiphase Rachford-Rice solver, and the following steps are successive substitution, accelerated successive substitution, and stability analysis.

The final problem during the formal part of the course (first two weeks) is to write an efficient solver for a mixture of dimerizing and cross-dimerizing components described by the ideal gas law. Essentially, this is the type of solver that is required in SAFT-type association models.

The participants are graded based on a report they write afterwards relating to an individual problem they solve (in teams of two). One example is given below:

> *"Correlation of VLE frequently requires the calculation of the equilibrium curve for binary mixtures at fixed temperature (Pxy-curves) or at fixed pressure (Txy-curves). Write a program for automatic calculation of such equilibrium curves. The program should be capable of*

TABLE 7

Types of Phase Equilibria and Choice of Thermodynamic Models for Specific Applications

Application (*e.g.* separation process)	**Systems**	**Phase Equilibria Types**	**Models (tools)**
Distillation/Absorption	hydrocarbons gases, non-polars	VLE, GLE	cubic EoS (vdW1f)
—	polars incl. gas/polars	VLE, GLE high pressures	cubic EoS (EoS/G^E rules e.g. MHV2, PSRK LCVM)
—	—	low pressure VLE & LLE	act. coef. models (van Laar, Wilson, NRTL, UNIQUAC, UNIFAC, RST)
—	polars, associating	multicomponent (V)LLE	UNIQUAC, CPA, PC-SAFT
Azetropic and Extractive Distillation	Polar, associating,...	VLE and LLE	UNIQUAC, CPA, PC-SAFT
Extraction	polars, associating water	LLE	UNIQUAC, CPA, PC-SAFT
Polymers	solutions, blends gas/polymers, etc.	VLE (act.coefs.), GLE, LLE, SLE, etc.	solubility parameters, FH, UNIFAC-FV, Entropic-FV, cubic EoS (vdW1f & EoS/GE), PC-SAFT, various complex EoS e.g. Sanchez-Lacombe
Environmental thermodynamics	water, air, complex pollutants/ chemicals, biota	Kow, infinite dilution act. coefs., VLE/LLE, SLE	UNIFAC-water, Kow-correlations, advanced models
Many others	solids, electrolytes, pharmaceuticals,	SLE, LLE, SSLLE, SGE	all the above and more…
(adsorption, SCFE, crystallization, complex products,…)	biomolecules, surfactants, colloids,…	—	—

Abbreviations

act.coef. = activity coefficient
EoS = equation of state
CPA = Cubic Plus Association
FH = Flory-Huggins
FV = Free-Volume
GLE = gas-liquid equilibria
Kow = octanol-water (partition coefficient)
LCVM = lineac combination Vidal and Michelsen mixing rules
LLE = liquid-liquid equilibria
MHV2 = modified Huron-Vidal mixing rule
NRTL = Non-random two-liquid activity coefficient model
PC-SAFT = Perturbed Chain Statistical Associating Fluid Theory
PSRK = predictive Soave-Redlich-Kwong EoS
RST = regular solution theory
SCFE = Supercritical Fluid Extraction
SGE = solid-gas equilibria
SLE = solid-liquid equilibria
vdW1f = van der Waals one fluid mixing rules
VLE = vapor-liquid equilibria
UNIFAC = Uniquac Functional activity coefficient
UNIQUAC = Universal quasichemical activity coefficient

calculating the equilibrium curve for mixtures in which one of the pure components is supercritical."

CONCLUDING REMARKS

Four different courses in Chemical Engineering Thermodynamics have been presented, fulfilling different needs and offered at different degree levels: Engineering Bachelor, B.Sc., M.Sc., and Ph.D. The context and learning objectives of the courses have been comparatively presented with special emphasis on the different teaching methods employed, *e.g.*, use of software at various levels and degrees of complexity. We consider it a problem that there is a lack of suitable textbooks that present chemical engineering thermodynamics in an applied, thermodynamic framework. Despite this difficulty, however, the very-positive evaluations of all the courses and other indicators (*e.g.*, increasing number of students) point out that the changes implemented in teaching chemical engineering thermodynamics at DTU have led to improved courses and enhanced both understanding and interest of students in chemical engineering thermodynamics.

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